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Description

GREASE COMPOSITION AND ROLLING DEVICE

Technical Field

The present invention relates to a grease composition particularly excellent in anti-flaking performance and anti-seizure performance in a wide temperature range of from a low temperature to a high temperature and having a low torque performance. Moreover, the invention relates to a rolling device such as a rolling bearing, a ball screw device, or a linear guide device into which such a grease composition is charged.

Background Art

In rolling bearings for use in motors and the like and ball screw devices and linear guide devices for use in machine tools and the like, a small torque, a maintenance-free property (durability for a long period of time), and the like characteristics are required for enhancing working efficiency. In these rolling devices, grease compositions have been generally used for lubrication. In order to satisfy such requirements, a lithium soap grease (e.g., "Multemp SRL" manufactured by

Kyodo Yushi Co., Ltd.) containing a low viscosity ester oil-based synthetic oil has been used. However, such a grease composition achieves a low torque but ester-based synthetic oil are generally insufficient in heat resistance and are problematic in seizure life.

Moreover, rolling bearings have widely been used in engine auxiliaries of automobiles, such as an alternator, but they have many chances to come into contact with water. Among the machine tools, some of them come into contact with water. Therefore, these rolling devices should be excellent in antirust properties. Thus, a sulfonate salt excellent in antirust properties is frequently added to a grease composition (e.g., see Japanese Patent Unexamined Publication JP-A-7-179879). However, the sulfonate salt has a problem that it promotes generation of hydrogen owing to degradation of a grease composition and is apt to induce flaking involving white texture change caused by the hydrogen (hereinafter referred to as "white texture flaking").

The invention is conducted in consideration of the above circumstances and an object of the invention is to provide a grease composition particularly maintaining a low torque over a wide temperature range of from a low temperature to a high temperature and further suppressing generation of white texture flaking as well as a rolling

device into which the above grease composition is charged and which works with a low torque, hardly induces white texture flaking, and is excellent in durability.

Disclosure of the Invention

In order to achieve the above object, the present invention provides a grease composition comprising a base oil having a dynamic viscosity at 40°C of 20 to 50 mm^2/s; a urea compound as a thickening agent in an amount of 8 to 30% by weight with respect to total weight of the grease; at least one antirust additive selected from carboxylic acids, carboxylate salts, and ester-based antirust additives in an amount of 0.1 to 10% by weight per single additive with respect to total weight of the grease and in an amount of 0.1 to 15% by weight in total of the additive with respect to total weight of the grease, and a rolling device into which the above grease composition is charged.

Brief Description of the Drawings

FIG. 1 is a sectional view illustrating one embodiment of a rolling bearing which is one of the rolling devices of the invention,

FIG. 2 is a graph illustrating the relationship between dynamic viscosity of a base oil and an flaking

life ratio obtained in Examples,

FIG. 3 is a graph illustrating the relationship between dynamic viscosity of a base oil and dynamic torque obtained in Examples,

FIG 4 is a graph illustrating the relationship between dynamic viscosity of a base oil and a seizure life ratio obtained in Examples,

FIG. 5 is a schematic block diagram illustrating a test apparatus for use in measurement of flaking generation probability,

FIG. 6 is a graph illustrating the relationship between an amount of zinc naphthenate added and flaking generation probability or a rust evaluation score obtained in Examples, and

FIG. 7 is a graph illustrating the relationship between an amount of an organometallic salt (ZnDTC) and flaking generation probability or seizure life time obtained in Examples.

Numeral 1 represents an inner ring, 2 represents an outer ring, 3 represents a ball, 4 represents a holder, and 5 represents a sealing member in the figures.

Best Mode for Carrying Out the Invention

The following will explain the present invention in detail.

[Grease Composition]

(Base Oil)

In the invention, the base oil for use in the grease composition is not particularly limited except that the dynamic viscosity at 40°C is from 20 to 50 mm^2/s. In order to secure torque performance at a low temperature and more surely avoid seizure which occurs since an oil film is hardly formed at a high temperature, the dynamic viscosity of the base oil at 40°C is preferably from 25 to 50 mm^2/s.

As specific examples usable as the base oil, there may be mentioned mineral oil-, synthetic oil-, or natural oil-based lubricating oil and the like. As the mineral oil-based lubricating oil, use can be made of those obtained by purifying mineral oil by suitably combining distillation under reduced pressure, oil-deasphalting, solvent extraction, hydrogenolysis, solvent dewaxing, sulfuric acid washing, clay purification, hydrogenative purification, and the like. As the synthetic oil-based lubricating oil, there may be mentioned hydrocarbon oil, aromatic oil, ester-based oil, ether-based oil, and the like. As the hydrocarbon oil, there may be mentioned normal paraffins, isoparaffins, poly-α-olefins such as polybutene, polyisobutyrene, 1-decene oligomers, and cooligomers of 1-decene with

ethylene, hydrogenated products thereof, and the like. As the aromatic oil, there may be mentioned alkylbenzenes such as monoalkylbenzenes and dialkylbenzenes, alkylnaphthalenes such as monoalkylnaphthalenes, dialkylnaphthalenes, and polyalkylnaphthalene, and the like. As the ester-based oil, there may be mentioned diester oil such as dibutyl sebacate, di-2-ethylhexyl sebacate, dioctyl adipate, diisodecyl adipate, ditridecyl adipate, ditridecyl glutamate, and methyl acetylcinolate, aromatic ester oil such as trioctyl trimellitate, tridecyl trimellitate, and tetraoctyl pyromellitate, further, polyol ester oil such as trimethylolpropane caprilate, trimethylolpropane pelargonate, pentaerythritol-2-ethylhexanoate, pentaerythritol pelargonate, furthermore, complex ester oil which are oligoesters of polyhydric alcohols with mixed fatty acids of dibasic acids and monobasic acids, and the like. As the ether-based oil, there may be mentioned polyglycols such as polyethylene glycol, polypropylene glycol, polyethylene glycol monoethers, and polypropylene glycol monoethers, phenyl ether oil such as monoalkyl triphenyl ether, alkyl diphenyl ether, dialkyl diphenyl ether, pentaphenyl ether, tetraphenyl ether, monoalkyltetraphenyl ether, and dialkyltetraphenyl ether, and the like. As the other synthetic lubricating base

oil, there may be mentioned tricresyl phosphate, silicone oil, perfluoroalkyl ethers, and the like. As the natural oil-based lubricating base oil, there may be mentioned oil-and-fat-based oil such as beef tallow, lard, soybean oil, rapeseed oil, rice bran oil, coconut oil, palm oil, palm kernel oil and hydrogenation products thereof. Among these lubricating oil, in view of the use in a wide temperature range of from a low temperature to a high temperature, ester-based synthetic oil, synthetic hydrocarbon oil, ether-based synthetic oil, and the like are preferred.

The lubricating oil mentioned above can be used singly or as a mixture obtained by suitably combining them and they are adjusted to a preferred dynamic viscosity as mentioned above.

(Thickening agent)

Any compound can be used without particular limitation as far as it is a urea compound However, in view of acoustic performance, long-term stability, and the like, a mixture of diurea compounds represented by the following general formulae (1) to (3) is preferred. In this connection, the blending amount of the thickening agent is from 8 to 30% by weight with respect to total weight of the grease. When the amount is less than 8% by weight, the form as grease cannot be formed or maintained

and when it exceeds 30% by weight, a low torque performance cannot be realized.

$$R_1-NH\overset{\overset{\displaystyle O}{\|}}{C}NH-R_2-NH\overset{\overset{\displaystyle O}{\|}}{C}NH-R_1 \qquad (1)$$

$$R_1-NH\overset{\overset{\displaystyle O}{\|}}{C}NH-R_2-NH\overset{\overset{\displaystyle O}{\|}}{C}NH-R_3 \qquad (2)$$

$$R_3-NH\overset{\overset{\displaystyle O}{\|}}{C}NH-R_2-NH\overset{\overset{\displaystyle O}{\|}}{C}NH-R_3 \qquad (3)$$

Wherein R_1 is a cyclohexyl group or an alkylcyclohexyl group having 7 to 12 carbon atoms, R_2 is a divalent aromatic ring-containing hydrocarbon group having 6 to 15 carbon atoms, and R_3 is an alkyl group having 8 to 20 carbon atoms.

Moreover, at the mixing, the above diurea compounds are mixed so that a ratio of [number of moles of R_1/(number of moles of R_1 + number of moles of R_3)] becomes from 0.1 to 1.0. When the value is less than 0.1, grease leakage increases and there is a possibility that the seizure life may be shortened. The ratio is

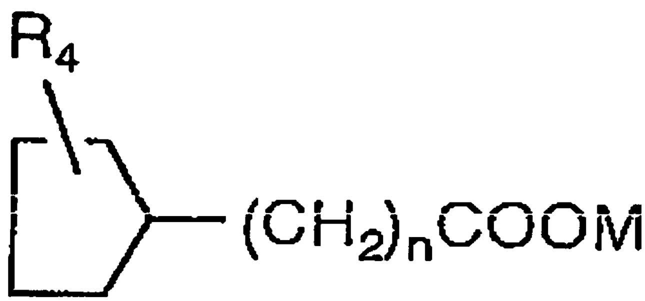
preferably from 0.2 to 0.9.

(Antirust additive)

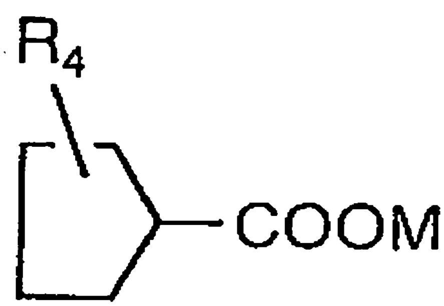
In order to impart antirust performance without generating white texture flaking, at least one antirust additive selected from carboxylic acids, carboxylate salts, and ester-based antirust additives is blended into the grease composition. These antirust additives do not promote generation of hydrogen involved in grease degenerative decomposition unlike sulfonate salts and can suppress the generation of white texture flaking. The amount of the antirust additive to be added is from 0.1 to 10% by weight per single additive with respect to total weight of the grease. When the amount is less than 0.1% by weight, impartment of the antirust performance is insufficient and when the amount exceeds 10% by weight, grease is softened and grease leakage tends to occur. In view of sufficient impartment of the antirust performance and grease leakage, the amount to be added is preferably from 0.25 to 5% by weight. Furthermore, total amount of the antirust additives is from 0.1 to 15% by weight.

Among the carboxylate salts, naphthenate salts are preferred. The naphthenate salts are not particularly limited as far as they are saturated carboxylate salts having a naphthene base. For example, there may be mentioned saturated monocyclic carboxylate

salts ($C_nH_{2n-1}COOM$), saturated polycyclic carboxylate salts ($C_nH_{2n-3}COOM$), aliphatic carboxylate salts ($C_nH_{2n+1}COOM$), and derivatives thereof. Moreover, as the monocyclic carboxylate salts, compounds represented by the following general formulae (4) and (5) can be exemplified:



(4)



(5)

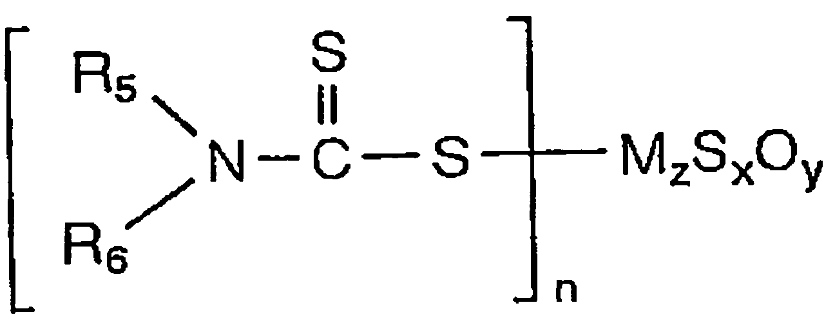
Wherein R_4 represents a hydrocarbon group and specifically, an alkyl group, an alkenyl group, an aryl group, an alkaryl group, or an aralkyl group, or the like may be mentioned; and M represents a metal element and specifically Co, Mn, Zn, Al, Ca, Ba, Li, Mg, Cu, or the like. These naphthenate salts may be used singly or as a suitable combination thereof.

Further, as a carboxylic acid salt, sccinic acid

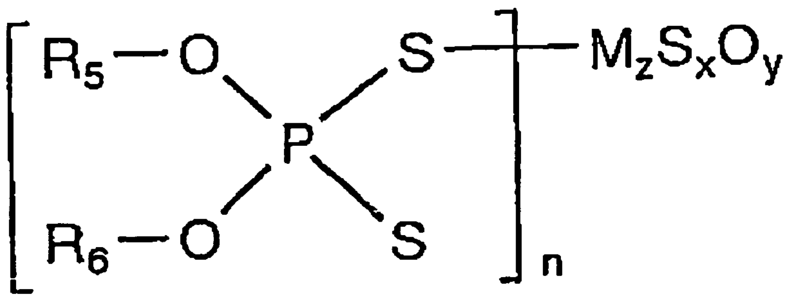
derivate is also preferable. As this succinic acid derivate, succinic acid, alkylscсinic acid, alkylsuccinic half ester, alkenylsuccinic acid, alkenylsuccinic half ester, succinic acid imido can be raised. These succinic acid derivates can be used singly or as a mixture obtained by suitably combining them.

(Other additives)

To the grease composition, if necessary, various additives hitherto known can be added. Among them, organometallic salts are additives effective for improving flaking performance. Among the organometallic salts, dialkyl dithiocarbamic acid(DTC)-based compounds shown in the following general formula (6) and dialkyl dithiophosphoric acid(DTP)-based compounds shown in the following general formula (7) can be suitably used:



(6)



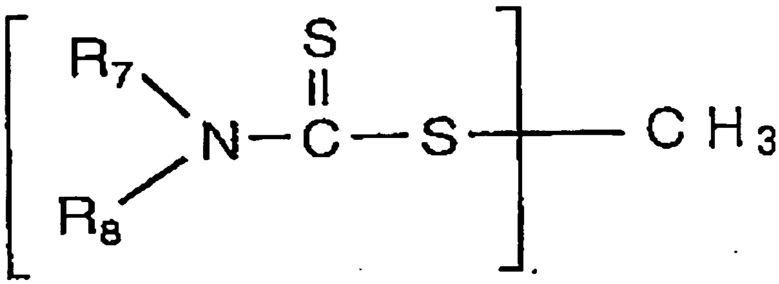
(7)

$n=2,3,4 \quad x,y,z=0,1,2,3,4$

Wherein M represents a metal species and specifically Sb, Bi, Sn, Ni, Te, Se, Fe, Cu, Mo, or Zn is used; R_5 and R_6 may be the same or different from each other and each represents an alkyl group, a cycloalkyl group, an alkenyl group, an aryl group, an alkylaryl group, or an arylalkyl group. Particularly preferred groups include a 1,1,3,3-tetramethylbutyl group, a 1,1,3,3-tetramethylhexyl group, a 1,1,3-trimethylhexyl group, a 1,3-dimethylbutyl group, 1-methylundecane group, a 1-methylhexyl group, a 1-methylpentyl group, a 2-ethylbutyl group, a 2-ethylhexyl group, a 2-methylcyclohexyl group, a 3-heptyl group, a 4-methylcyclohexyl group, an n-butyl group, an isobutyl group, an isopropyl group, an isoheptyl group, an isopentyl group, an undecyl group, an eicosyl group, an ethyl group, an octadecyl group, an octyl group, a cyclooctyl group, a cyclododecyl group, a cyclopentyl

group, a dimethylcyclohexyl group, a decyl group, a tetradecyl group, a docosyl group, a dodecyl group, a tridecyl group, a trimethylcyclohexyl group, a nonyl group, a propyl group, a hexadecyl group, a hexyl group, a henicosyl group, a heptadecyl group, a heptyl group, a pentadecyl group, a pentyl group, a methyl group, a tert-butylcyclohexyl group, a tert-butyl group, a 2-hexenyl group, a 2-methallyl group, an allyl group (changed from "an aryl group" since it is overlapped with the above aryl group), an undecenyl group, an oleyl group, a decenyl group, a vinyl group, a butenyl group, a hexenyl group, a heptadecenyl group, a tolyl group, an ethylphenyl group, an isopropylphenyl group, a tert-butylphenyl group, a sec-pentylphenyl group, an n-hexylphenyl group, a tert-octylphenyl group, an isononylphenyl group, an n-dodecylphenyl group, a phenyl group, a benzyl group, a 1-phenylmethyl group, a 2-phenylethyl group, a 3-phenylpropyl group, a 1,1-dimethylbenzyl group, a 2-phenylisopropyl group, a 3-phenylhexyl group, a benzhydryl group, a biphenyl group, and the like and also these groups may have an ether bond.

Moreover, as the other organometallic salts, use can be made of ashless dithiocarbamates such as methylene-bis-alkyl dithicarbamate represented by the following general formula (8):



(8)

Wherein R_7 and R_8 each represents a hydrocarbon group having 1 to 18 carbon atoms and R_7 and R_8 may be the same or different from each other.

The above organometallic salts may be used singly or as a combination of two or more thereof. In this connection, no limitation exists for the combination. Moreover, the organometallic salt is added in an amount of 0.1 to 10% by weight with respect to total weight of the grease in the case that it is used singly. The organometallic salt has an action of forming a reaction film in minute spaces to suppress the white texture flaking but this action is not sufficiently exhibited when the amount added is less than 0.1% by weight. On the other hand, when the amount added exceeds 10% by weight, there is a possibility of deteriorating seizure performance through induction of excessive reaction between the organometallic salts. Furthermore, the organometallic salt is expensive and hence the case is

not preferred also economically. Moreover, in the case that the organometallic salts are used in combination, the amount of each organometallic salt is from 0.1 to 10% by weight as in the case of single use but the total amount is preferably 15% by weight or less. When the amount added is more than 15% by weight, blending ratios of the base oil, the thickening agent, and the antirust additive relatively decrease and thus respective effects become insufficient.

(Production process)

The process for producing the grease composition is not particularly limited. An antirust additive and furthermore, if necessary, various additives such as organometallic salts and ashless dithiocarbamate may be added to a grease composition obtained by reacting a thickening agent in the base oil and the whole may be thoroughly mixed and homogeneously dispersed. At the time when the treatment is conducted, heating is also effective.

Moreover, consistency of the above grease composition is preferably NLGI (National Lubricating Grease Institute) No. 1 to 3.

(Rolling device)

The invention relates to a rolling device into which the above grease composition is charged. The

rolling device is not limited and a rolling bearing, a ball screw device, a linear guide device, and the like can be exemplified. With regard to any rolling devices, the constitution is not limited and it may be known one. For example, as a rolling bearing, a ball bearing shown in FIG. 1 can be exemplified. The rolling bearing shown in the figure has a constitution wherein there are provided an outer ring 2 having an outer ring raceway 2a on its inside surface, an inner ring 1 having an inner ring raceway 1a on its outside surface, a plurality of rolling elements, balls 3 provided between the outer ring raceway 2a and the inner ring raceway 1a in a freely rollable manner, and a holder 4 which holds a plurality of the balls 3 in a freely rollable manner, the above grease composition G is charged into a space 6 between the outer ring raceway 2a and the inner ring raceway 1a, and a space between the inner ring 1 and the outer ring 2 is sealed by a sealing member 5 fixed to a seal groove 2b of the outer ring 2.

In this connection, the amount of the grease composition to be charged is suitably selected according to the kind of rolling devices.

Examples

The following will specifically describe the

invention with reference to Examples and Comparative Examples but the invention is not limited thereto.

Examples 1 and 2, Comparative Examples 1 to 6

Test greases were prepared with formulations shown in Table 1. With regard to Examples 1 and 2 and Comparative Examples 2 to 6, a base oil mixed with a diisocyanate was reacted with the same base oil mixed with an amine and the whole was stirred under heating to obtain a semi-solid material, an antirust additive (zinc naphthenate, a succinate ester, barium sulfonate) and/or an organometallic salt (zinc dialkyldithiocarbamate: ZnDTC, zinc dialkyldithiophosphate: ZnDTP), which were already solved in the base oil, were added to the semi-solid material, and the whole was thoroughly stirred and, after gradual cooling, was passed through a roll mill to obtain a grease. With regard to Comparative Example 1, stearic acid and lithium hydroxide were reacted in a base oil to form a lithium soap, barium sulfonate was added after cooling to room temperature, and the whole was thoroughly stirred and then was passed through a roll mill to obtain a grease. Thereafter, test greases were subjected to (1) white flaking life test, (2) dynamic torque test, and (3) seizure life test.

Table 1

	Example 1	Example 2	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6
Thickening agent	diurea compound		Li soap	diurea compound				
Amount of thickening agent	13% by weight	20% by weight	11% by weight	13% by weight			20% by weight	
$R_1/(R_1+R_3)$	0.3	1.0	-	0.3			1.0	
Base oil	PAO	PAO+ether oil	ester oil	PAO			PAO+ether oil	
Dynamic viscosity of base oil	20 to 50	20 to 50	26	30	15	60	15	60
Zinc naphthenate	1% by weight	2% by weight	-	-	1% by weight	1% by weight	2% by weight	2% by weight
Succinate ester	1% by weight	2% by weight	-	-	1% by weight	1% by weight	2% by weight	2% by weight
ZnDTC	1% by weight	-	-	-	1% by weight	1% by weight	-	-
ZnDTP	-	1% by weight	-	-	-	-	1% by weight	1% by weight
Barium sulfonate	-	-	1% by weight	2% by weight	-	-	-	-
Mixed consistency	240 to 250	260 to 270	260	235	251	240	280	271

Note 1) Unit of dynamic viscosity of base oil: mm^2/s (40°C)

(1) White flaking life test

Each of the above test greases was charged in an amount of 2.3 g into a single row deep groove ball bearing fitted with a contact rubber seal having an inner diameter of 17 mm, an outer diameter of 47 mm, and a width of 14 mm to prepare a test bearing. Then, the test bearing was continuously rotated under conditions of an inner ring rotation speed of 10500 min^{-1}, room temperature atmosphere, and a radial load of 1320 N. When flaking was induced on the running surface of the outer ring to generate vibration, the rotation was stopped and time passed until that time was measured. The test was repeated five times per each of the test greases and an average value was regarded as white flaking life. The results are shown in FIG. 2, the results being shown as relative values to the white flaking life of the test grease of Comparative Example 2.

From FIG. 2, among the test greases wherein a diurea compound is used as a thickening agent and zinc naphthenate and a succinate ester were blended, there is a tendency that white flaking life increases as the dynamic viscosity of the base oil increases and it is found that the life is almost saturated in the range exceeding 50 mm^2/s (40°C). Moreover, when the dynamic viscosity of the base oil is less than 20 mm^2/s (40°C), an

improving effect on the white flaking life is hardly observed.

(2) Dynamic torque test

Each of the above test greases was charged in an amount of 3.4 g into a single row deep groove ball bearing fitted with a non-contact rubber seal having an inner diameter of 25 mm, an outer diameter of 62 mm, and a width of 17 mm (see FIG. 1) to prepare a test bearing. Then, dynamic torque was measured when the test bearing was continuously rotated for 30 minutes under conditions of an inner ring rotation speed of 3600 min^{-1}, a bearing temperature of 30°C, a radial load of 30 N, and an axial load of 60 N.

The results were shown in FIG. 3 and it is found that an acceptance criterion of 0.1 N·m or less is satisfied when the dynamic viscosity of the base oil falls within the range of 50 mm^2/s (40°C) or less

(3) Seizure life test

Each of the above test greases was charged in an amount of 2.0 g into a single row deep groove ball bearing fitted with a non-contact rubber seal having an inner diameter of 25 mm, an outer diameter of 62 mm, and a width of 17 mm (see FIG. 1) to prepare a test bearing. Then, the test bearing was continuously rotated under conditions of an inner ring rotation speed of 10000 min^{-1},

a bearing temperature of 120°C, and a radial load of 98 N. When the outer ring temperature reached 150°C due to seizure, the rotation was stopped and time passed until that time was measured. The test was repeated four times per each of the test greases and an average value was regarded as seizure life. The results are shown in FIG. 4, the results being shown as relative values to the seizure life of the test grease of Comparative Example 1.

From FIG. 4, it is found that seizure life increases as the dynamic viscosity of the base oil increases and the life is almost saturated in the range exceeding 50 mm^2/s (40°C). Moreover, when the dynamic viscosity of the base oil is less than 20 mm^2/s (40°C), an improving effect on the seizure life is hardly observed.

From the above test results, it is found that the grease compositions obtained by adding an urea compound as a thickening agent and zinc naphthenate or a succinate ester as an antirust additive to a base oil having a dynamic viscosity of 20 to 50 mm^2/s (40°C) according to the invention hardly induces white texture flaking and seizure at a high temperature and exhibits a low torque.

(4) Verification of blending amount of antirust additive

A base grease containing 13% by weight of a diurea compound ($R_1/(R_1+R_3) = 0.3$) and 1% by weight of ZnDTC in a poly-α-olefin having a dynamic viscosity of 40

mm^2/s (40°C) was prepared and zinc naphthenate was added to the base grease with changing the amount of the salt to be added, whereby test greases were obtained. Then, each of the test greases was charged in an amount of 2.3 g into a single row deep groove ball bearing with a contact rubber seal having an inner diameter of 17 mm, an outer diameter of 47 mm, and a width of 14 mm to prepare a test bearing and flaking generation probability was determined using a test apparatus shown in FIG. 5. In this connection, the test apparatus shown in the figure has a constitution that the inner ring of a test bearing 75 was fitted to an edge of a shaft 70 supported by one pair of supporting bearings 71, 71, furthermore its outer ring is fixed to a holder 72, and rotation from a motor (not shown in the figure) is transmitted to the test bearing 75. The test was conducted under the same conditions as in the above (1) white flaking life test.

Moreover, the same test grease was charged in an amount of 2.3 g into a single row deep groove ball bearing with a contact rubber seal having an inner diameter of 17 mm, an outer diameter of 47 mm, and a width of 14 mm to prepare a test bearing. After it was rotated at 1800 min^{-1} for 1 minute, 0.5 mL of 0.5% by weight of saline was introduced into the bearing and then the bearing was rotated at 1800 min^{-1} for another 1 minute.

After the test bearing was allowed to stand under conditions of 52°C and 100% RH for 48 hours, the test bearing was dismantled and a rusting state of each track surface of the inner and outer rings was observed. Evaluation was conducted according to the following standards and a score of 2 or less was regarded to be acceptable.

<Rust evaluation score>

1: no rust

2: three small rust points or less

3: four small rust points or more

Results of the flaking generation probability and rust evaluation score are shown in FIG. 6. It is found that the generation of the white texture flaking and the rust generation are both suppressed when the amount of zinc naphthenate added falls within the range of 0.1 to 10% by weight.

(5) Verification of blending amount of organometallic salt

A base grease containing 13% by weight of a diurea compound ($R_1/(R_1+R_3) = 0.3$), 1% by weight of zinc naphthenate, and 1% by weight of a succinate ester in a poly-α-olefin having a dynamic viscosity of 40 mm^2/s (40°C) was prepared and ZnDTC was added to the base grease with changing the amount thereof to be added, whereby

test greases were obtained. Then, the flaking generation probability was determined in the same manner as above. Furthermore, the above (3) seizure life test was conducted.

Results of the flaking generation probability and rust evaluation score are shown in FIG. 7 and it is found that the white texture flaking generation is suppressed when the amount of zinc naphthenate added falls within the range of 0.1 to 10% by weight and the seizure life is also improved at the same time.

Industrial Applicability

As described in the above, according to the invention, there is obtained a grease composition and rolling device having a good antirust property, suppressing generation of white texture flaking, and further having excellent anti-seizure performance.